Anodes-Nanoscale Heterostructures and Thermoplastic Resin Binders: Novel Li-ion Anode Systems

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2013 U.S. DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Program
Annual Merit Review and Peer Evaluation Meeting
May 13-17, 2013

Project ID #: ES061

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Overview

- **Timeline**
  - Start: Jan 2012
  - Finish: December 2012
  - 100% complete
- **Budget**
  - Total project funding
    - $1,082.7K
  - Funding received in FY11
    - $310.33K
  - Funding for FY12
    - $330.8K
  - Funding for FY 13
    - $330.8K

- **Barriers**
  - ***Performance***: **Low specific energy and energy density, poor rate capability**
  - ***Life***: **Poor cycle life and coulombic efficiency**
  - ***Cost***: **High cost of raw materials and materials processing**
- **Targets for PHEV (2015)**
  - ➢ **Available Energy: 3.5-11.6 kWh**
  - ➢ **Cycle life: 3,000-5,000 deep discharge**
  - ➢ **Recharge rate : 1.4-2.8 kW**
- **Partners/Collaborators/Students**
  - **Industries**
    - Ford Motor Company
  - **National Laboratory**
    - Dr. A. Manivannan, NETL
    - Dr. Vincent Battaglia, LBNL
  - **Other Universities**
    - Dr. Spandan Maiti, University of Pittsburgh
  - **Research Faculty/Students**
    - Dr. Moni Kanchan Datta, Univ. of Pittsburgh
    - Rigved Epur, Univ. of Pittsburgh

Objectives of this Study
Jan 2012-Dec 2012

- Identify new alternative nanostructured anode materials to replace synthetic graphite that will provide higher gravimetric and volumetric energy density
- Similar or lower irreversible loss (≤15%) in comparison to synthetic graphite
- Similar or better coulombic efficiency (≥99.9%) in comparison to synthetic graphite
- Similar or better cyclability and calendar life in comparison to synthetic graphite
- Investigate Microcrystalline (μm-Si), Nano-crystalline (*nc*-Si), Nanoparticle (*np*-Si) and amorphous Si (*a*-Si) based nanocomposite anodes
- Improve the **specific capacity, available energy density, rate capability and cycle life** of nano-structured and amorphous Si based anode materials
- Identify new ***elastomeric thermoplastic binders*** capable of binding the active materials preventing de-lamination

Milestones

Month/Year	Milestones or Go/No-Go Decision
March 2012	Milestone: Electrodeposition of amorphous Si anode with capacity **>1300 mAh/g** and excellent stability (fade=0.016% for 100 cycles)
June 2012	Milestone: Improved cycling stability using Interface Control Agent (ICA) for CNT/Si heterostructures with **85% capacity retention** at end of 75 cycles
August 2012	Milestone: Developed a scalable method for making **hollow Si nanostructures** with high capacity (**1800 mAh/g**), cycling stability, rate capability and columbic efficiency
October 2012	Milestone: Characterize the hetero-structures for structure and composition using electron microscopy techniques such as, SEM, TEM and HREM
December 2012	Milestone: Identified a low cost high strength polymer binder showing **improved adhesion** to Si/C composite

Si: Silicon, **C**: Graphite or Carbon, **CNT**: Carbon nanotube

Approach

- Explore ***Si and carbon/CNT*** based nanocomposite anode
  - Explore ***novel low cost approaches*** to generate **hollow Silicon structures**, Si/C and Si/CNT composite comprising microcrystalline (μm-Si), nanocrystalline (*nc*-Si), nanoparticle (*np*-Si) or amorphous Si (*a*-Si) and a variety of carbon precursors:
    - ***Electro-deposition***
    - ***Chemical vapor deposition (CVD)***
    - ***High energy mechanical milling (HEMM)***
    - ***High voltage solution process (HVSP)***
    - ***Fluidized bed reactor (FBR)***
- Explore **interface control agents (ICA)** to improve cyclability and coloumbic efficiency in CNT/Si based heterostructres
- Explore **suitable surface control additives (SCA) and surface electron conducting additives (SECA)** in Si/C nanocomposite which will ***reduce 1st cycle irreversible loss (FIR) and improve the coulombic efficiency (CE)*** in subsequent cycles
  - **Coating of Si/C composite** with suitable element or compound surface control additives (SCA) ***to improve CE and cycling stability***.
  - Use of highly **conductive additives to improve CE**.
- Explore high strength, high ductility ***elastomeric thermoplastic binders*** to bind the active materials
- Full cell and long cycling tests:
  - ***Coin cell and pouch cell*** configuration with suitable cathode

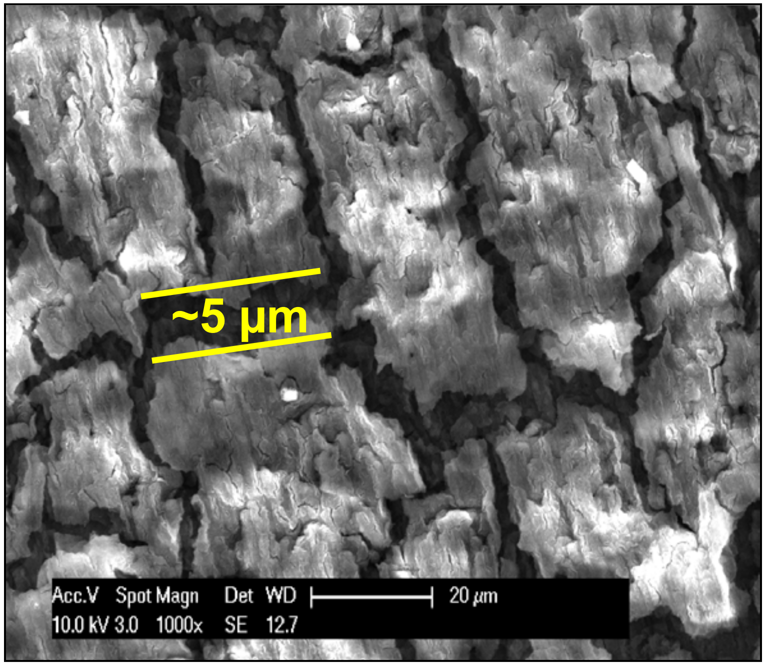
Technical accomplishments (FY-12)

Amorphous Si by Electrodeposition from Silicon Halides

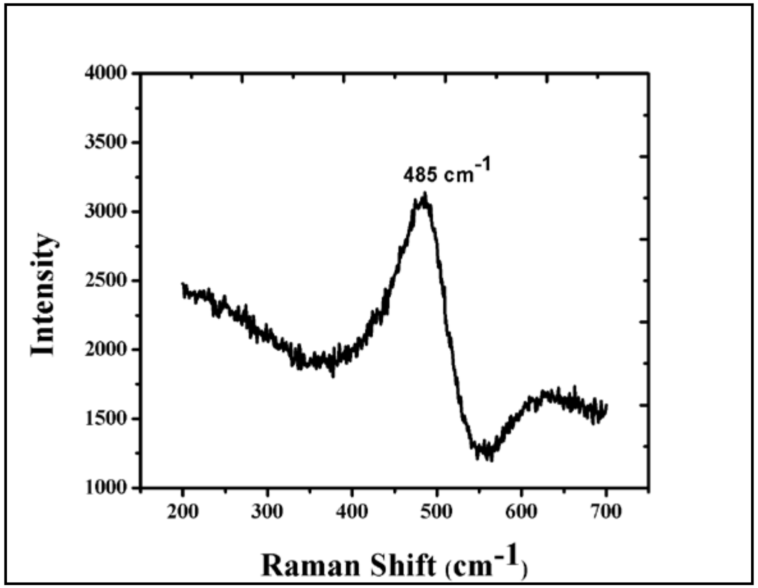
Working Electrode: Cu foil, Counter and Reference electrode: Pt
Electrolyte: 0.5M $SiCl_4$ + 0.1M Tetrabutyl ammonium chloride in propylene carbonate

- **Applied Current Density: -1mA/cm^2 , Deposition Time: 1h**

SEM (as deposited film)



Raman Spectra (633 nm laser)

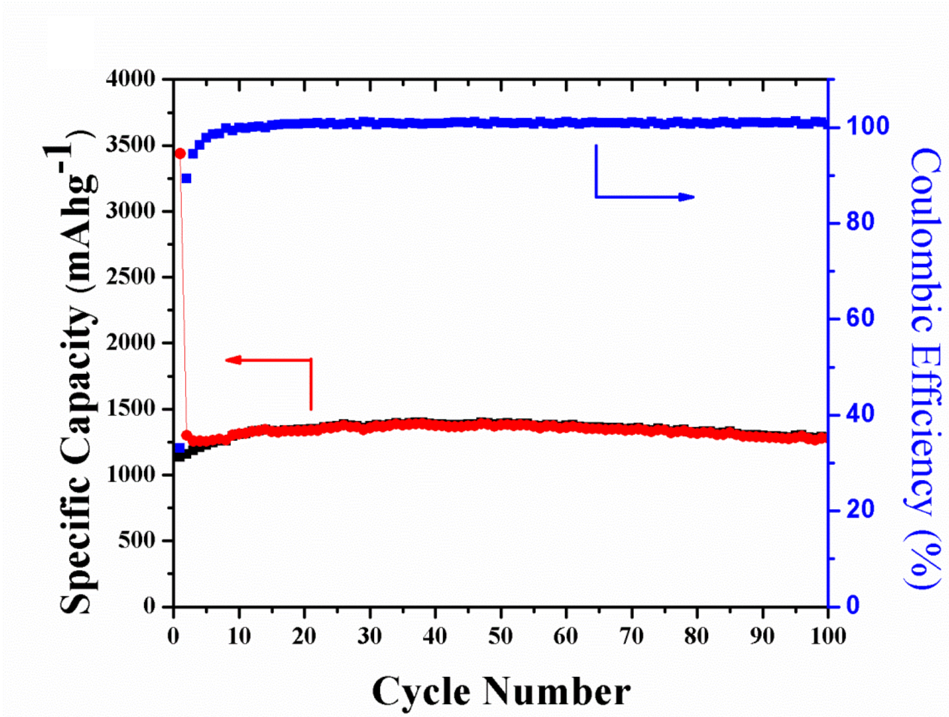


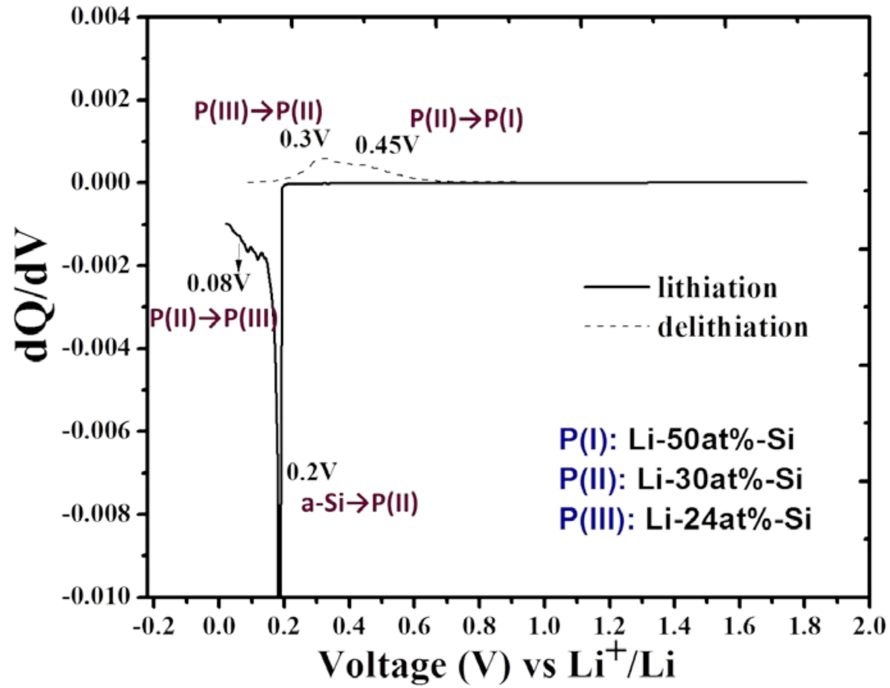
- **Broad peak at 480 cm^{-1} → a-Si**

- **Electrodeposited *a*-Si film exhibits cracked morphology optimized by applied current conditions. Si islands range from 10 to 20 µm in size**
- **Finite spacing (~5 µm) between islands allows for volume expansion during lithiation**

Technical accomplishments (FY-12)

Amorphous Si by Electrodeposition from Silicon Halides





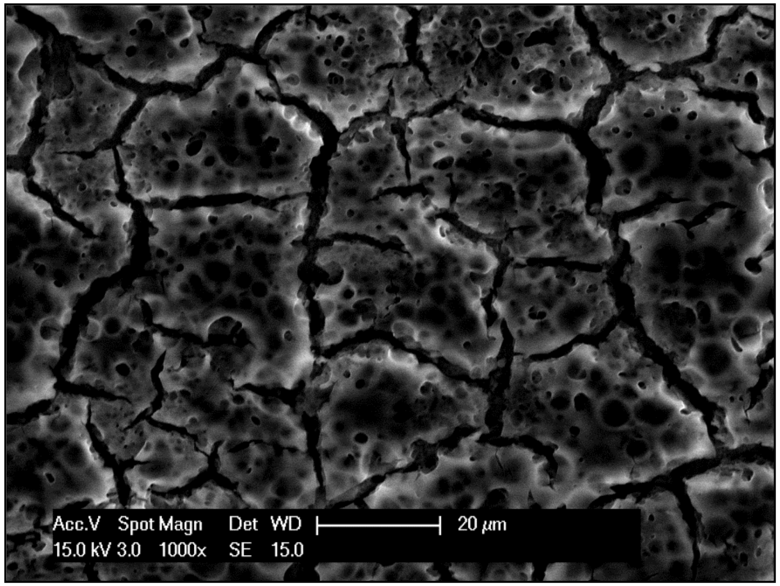
Electrolyte: 1M $LiPF_6$ in EC:DEC=1:2 (v:v)
Current rate: **400 mA/g**, (C/5 rate), **Voltage:** 0.02– 1.2 V
Loading: **0.3-0.5 mg/cm^2,**
No binders or **conductive additives** were used

- 1st discharge: **3400 mAh/g, 1st Charge:** **1150** mAh/g
- **FIR loss: 65%, Large IR loss due to surface oxide layer (SiO_x) and SEI formation**
- **Coulombic Efficiency**: **99.5%**
- **Stable reversible capacity of 1300 mAh/g for 100 cycles, 0.016% loss/cycle** at end of 100 cycles
- **Explore deposition and coating of conductive additives** to reduce the FIR

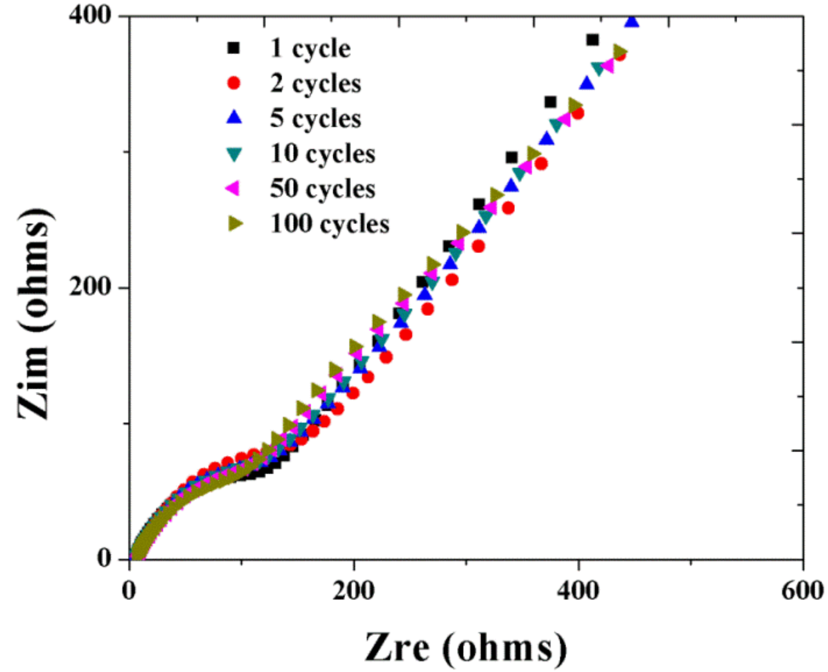
Technical accomplishments (FY-12)

Amorphous Si by Electrodeposition from Silicon Halides

SEM after 100 cycles



Impedance spectra



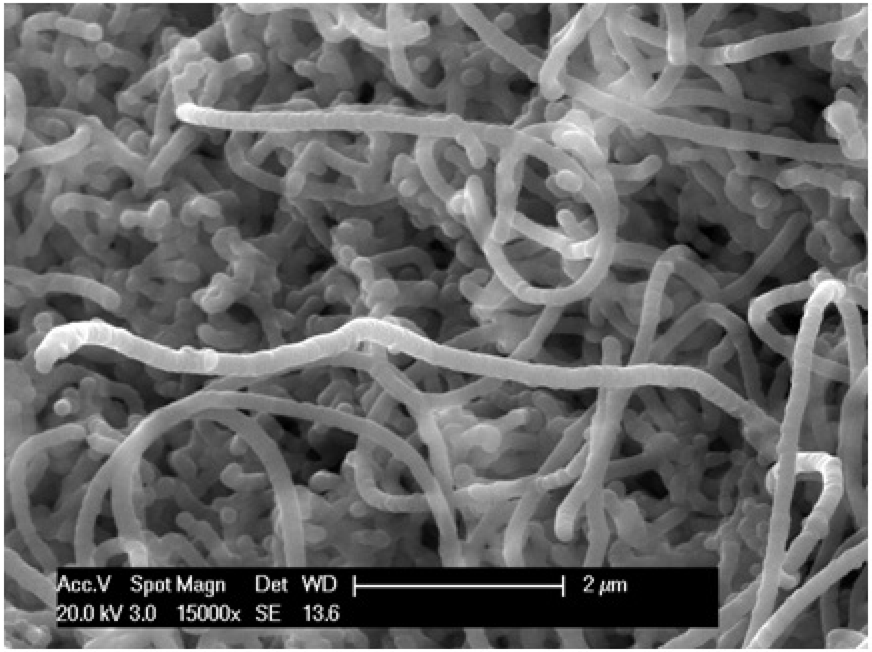
No significant change of surface morphology after **100 cycles**

- **Impedance taken at end of delithiation step (OCV: 1.2V vs. Li^+/Li)**
- **Frequency range: 50 KHz to 100 mHz**
- **10 mV amplitude, No bias**

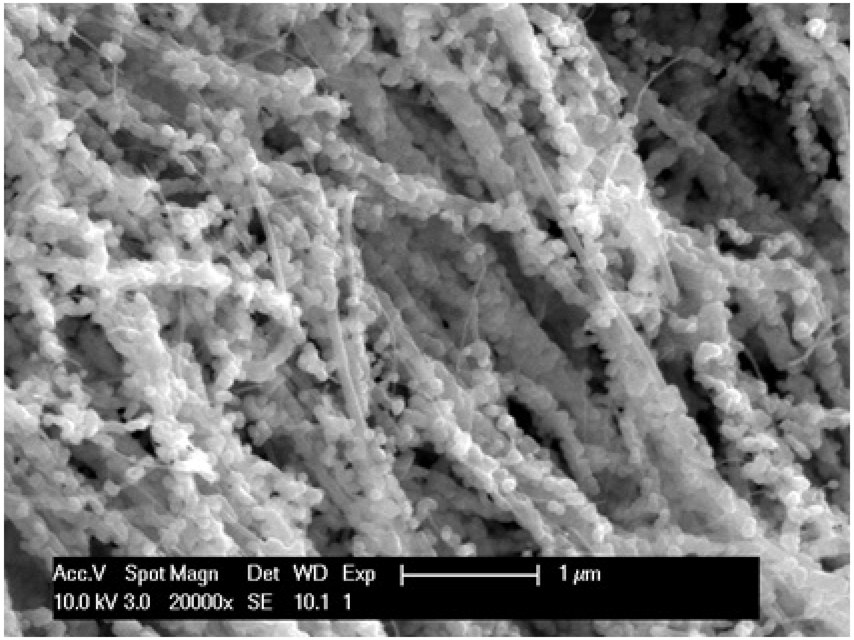
- **No change in shape of impedance plots at end of several stages**
- **No change in charge transfer resistance; No increase in film resistance**
- **No significant change of film structure after 100 cycles**

Technical accomplishments (FY-12)

Engineering of *nc*-Si/CNT Heterostructures by CVD



Silicon coated as uniform film on CNTs



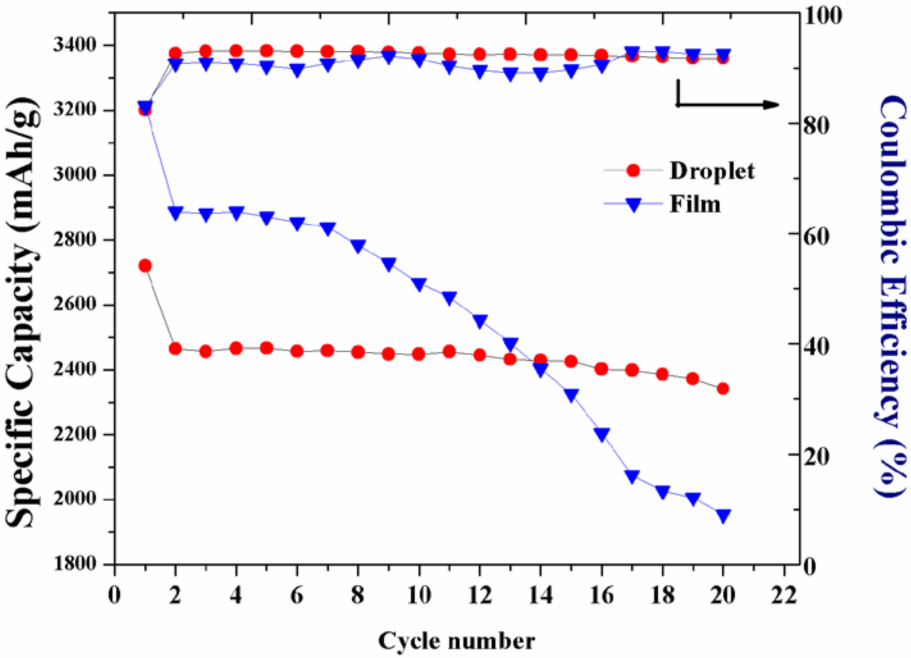
Silicon coated as droplets on CNTs

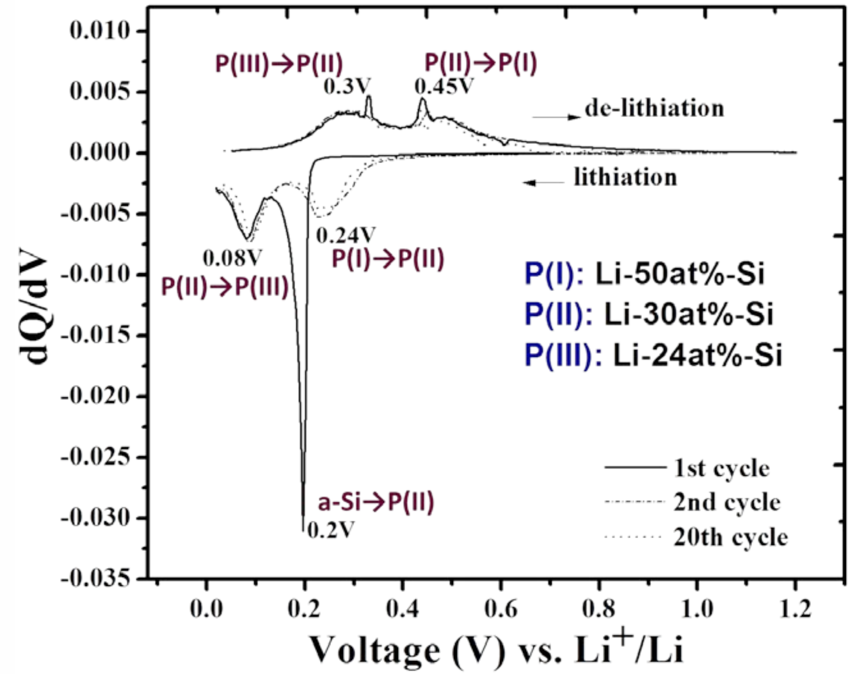
- **Film** – Higher partial pressure of SiH_4 (SiH_4:Ar=1:10)
- **Droplet** – Lower partial pressure of SiH_4 (SiH_4:Ar=1:30)
- Size of nanoscale silicon droplets : **40-60 nm**

Epur et al., 2012, *Electrochim Acta.* 85, pg-680

Technical accomplishments (FY-12)

Engineering of *nc*-Si/CNT Heterostructures by CVD





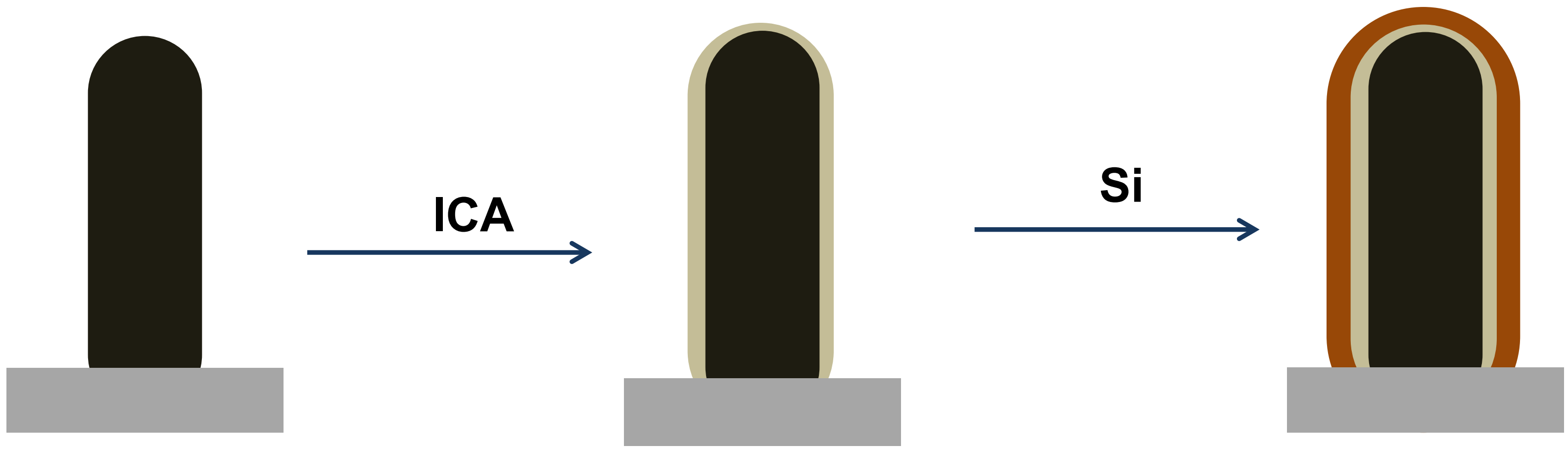
- Current: 100 mA/g (C/30), Voltage: 0.02 – 1.2V vs. Li^+/Li
- 1st discharge capacity: 3213 mAh/g (Film) & 2720 mAh/g (Droplet)
- First cyl IR loss: 10%, Coloumbic Efficiency: 95%

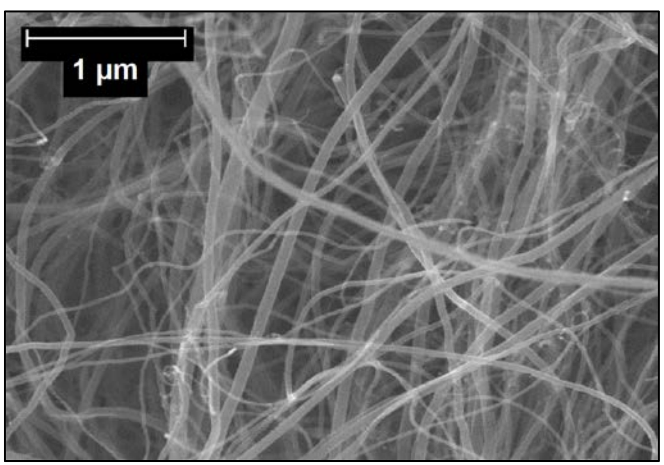
> ➢ Fade rate for film morphology: 1.61% loss/cycle
> ➢ Fade rate for droplet morphology: 0.25% loss/cycle
> ➢ Differential capacity plot shows amorphous nature of Si

Epur et al., 2012, *Electrochim Acta.* 85, pg-680

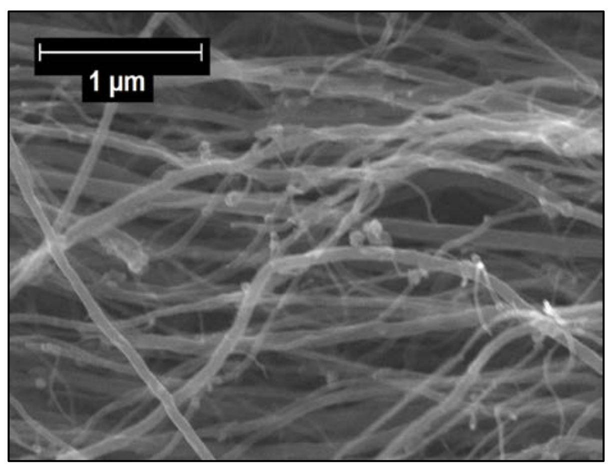
Technical accomplishments (FY-12)
CNT/Si/ICA – Interface Control

ICA – Interface control additive

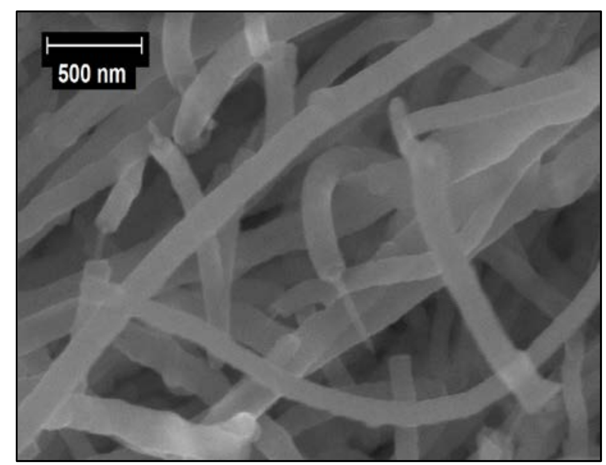




CNTs by CVD of m-xylene on quartz



ICA (10nm) deposition on CNT by eBeam



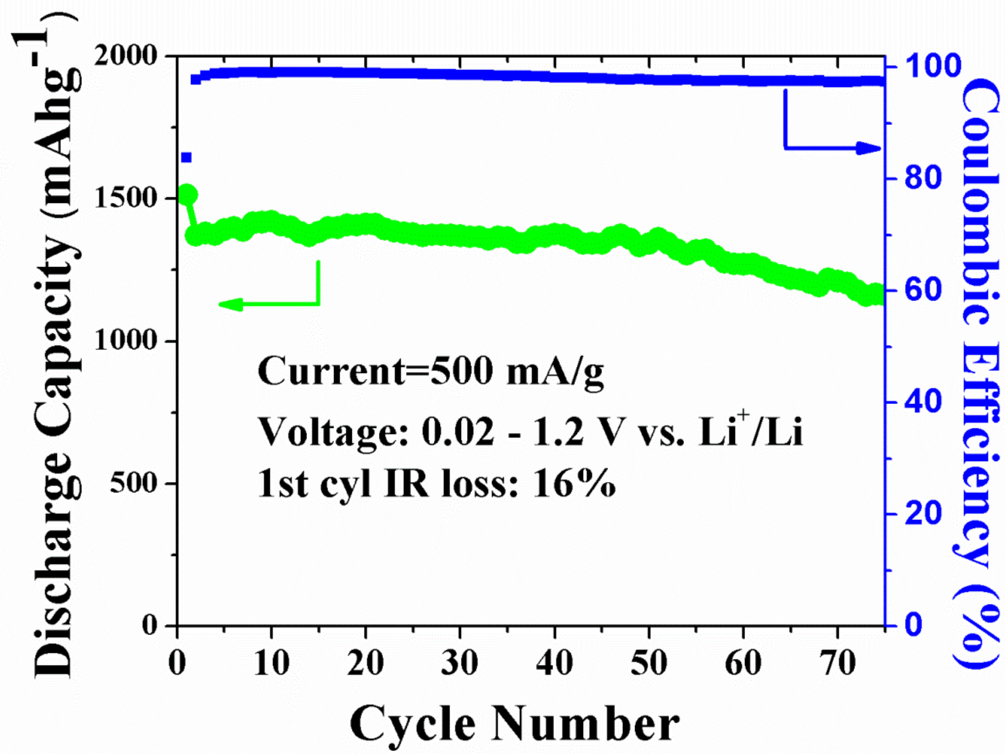
Si (50nm) by CVD of SiH_4

Technical accomplishments (FY-12)

CNT/Si/ICA heterostructures: Electrochemical Characterization

Electrolyte: 1M $LiPF_6$ in EC:DEC=1:2
Current rate: **500 mA/g**, (C/3 rate)
Voltage: 0.02– 1.2 V vs. Li^+/Li

- **Loading: 1.5 mg/cm²**

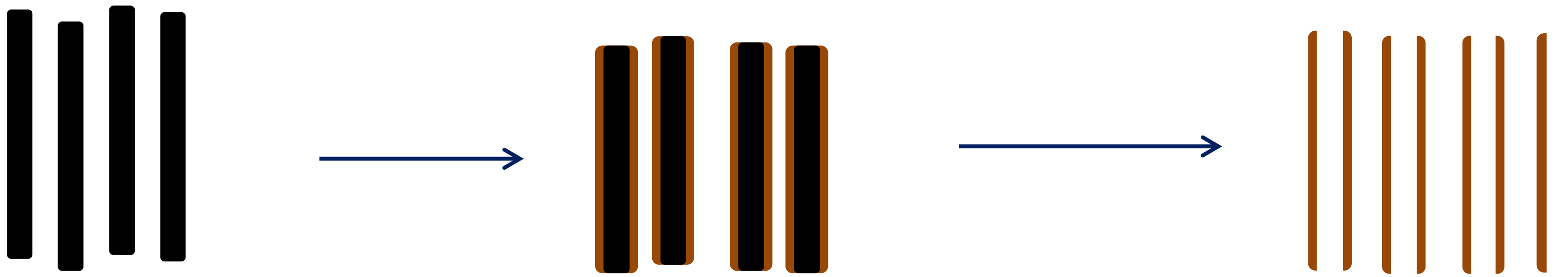


1st Discharge: 1512 mAh/g
1st Charge: 1370 mAh/g
First Cycle Irreversible loss: 16%
Coloumbic Efficiency: 98-99%

Capacity retention: **85%** at end of 75 cycles
Fade rate: **0.2%loss/cycle** at end of 75 cycles

Technical accomplishments (FY-12)

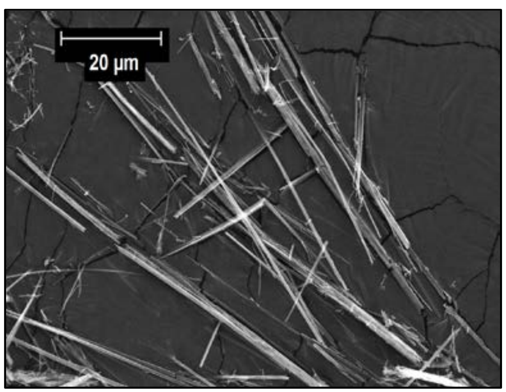
Large Scale Synthesis of Hollow Si Nanostructures

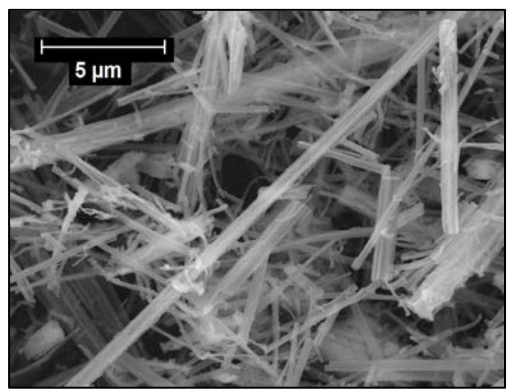


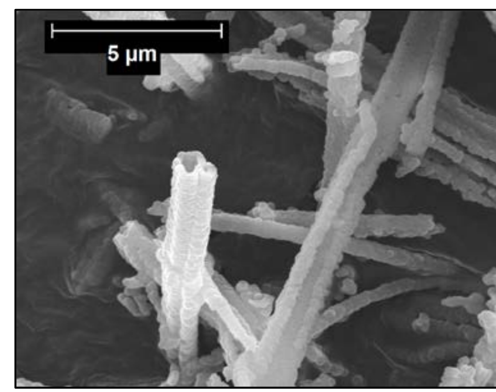
Sacrificial NanowireTemplate

Si Deposition by CVD

Dissolution of template to form hollow SiNTs





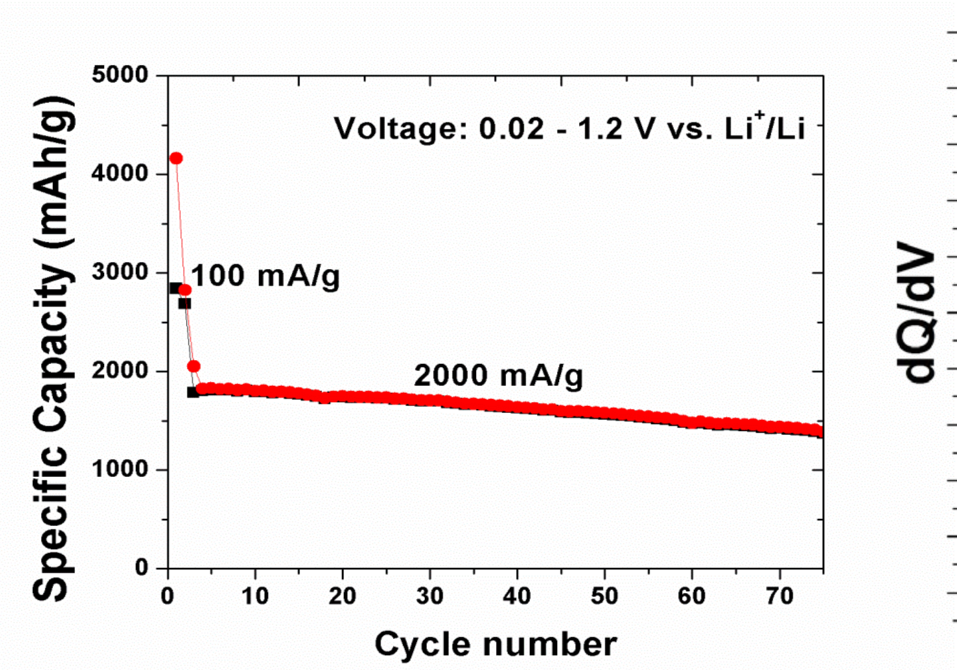


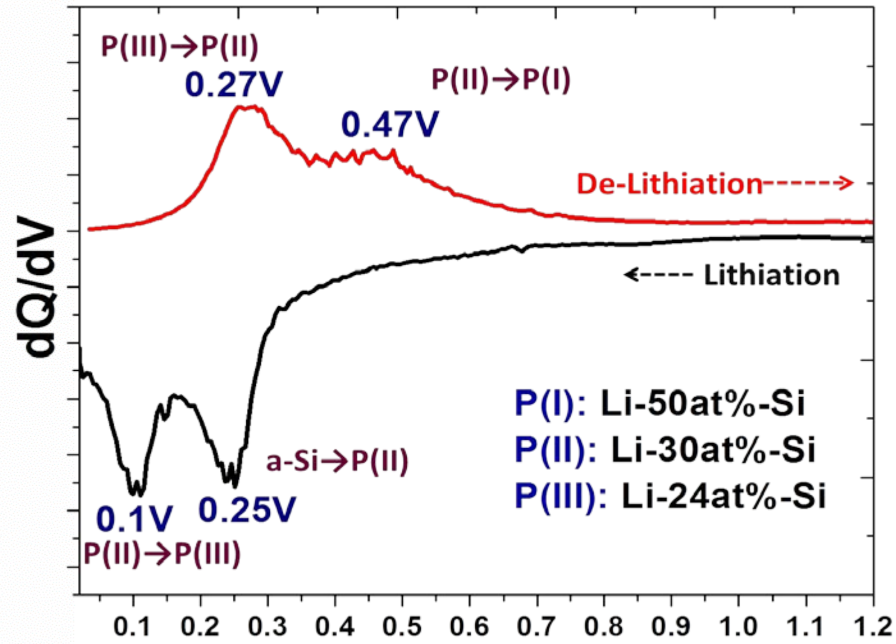
- **Diameters : 0.6-1 µm**
- **Length : 5-100 µm**

- Si coats uniformly on the template
- Form a core shell (Si) morphology
- Si coating thickness: **100-150nm**

Technical accomplishments (FY-12)

Si Hollow Structures: Electrochemical Characterization





- Lithiation potential corresponds to reaction with a-Si
- High capacity (**1800 mAh/g**) at high current rate (2A/g, 1C)
- **FIR loss: 25%, Coloumbic Efficiency: 99.5%**
- **Good cyclability: Capacity retention of 76% (after IR loss), 0.32% loss/cycle (calculated at end of 75 cycles)**
- **Loading: 1.21 mg/cm^2**

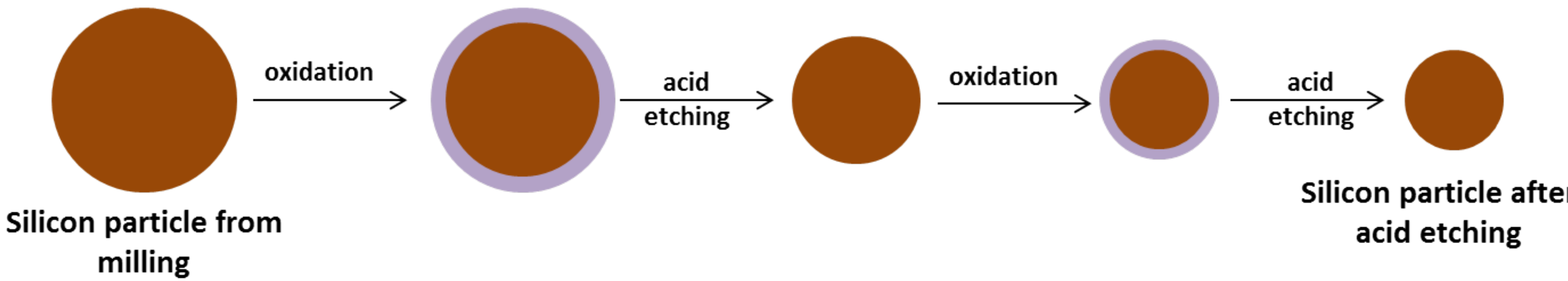
Future work:

Approach to decrease FIR ⟶ explore SCA and SECA coatings on Si hollow structures to decrease SEI formation

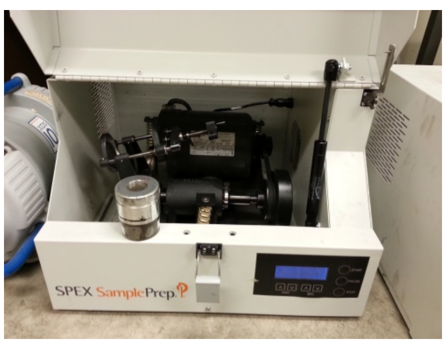
Technical accomplishments (FY-12)

Facile, High throughput Scalable Approach to

High Specific Surface Area Si (HSA-Si)



$$\boxed{MX + B \rightarrow Si + BX}$$



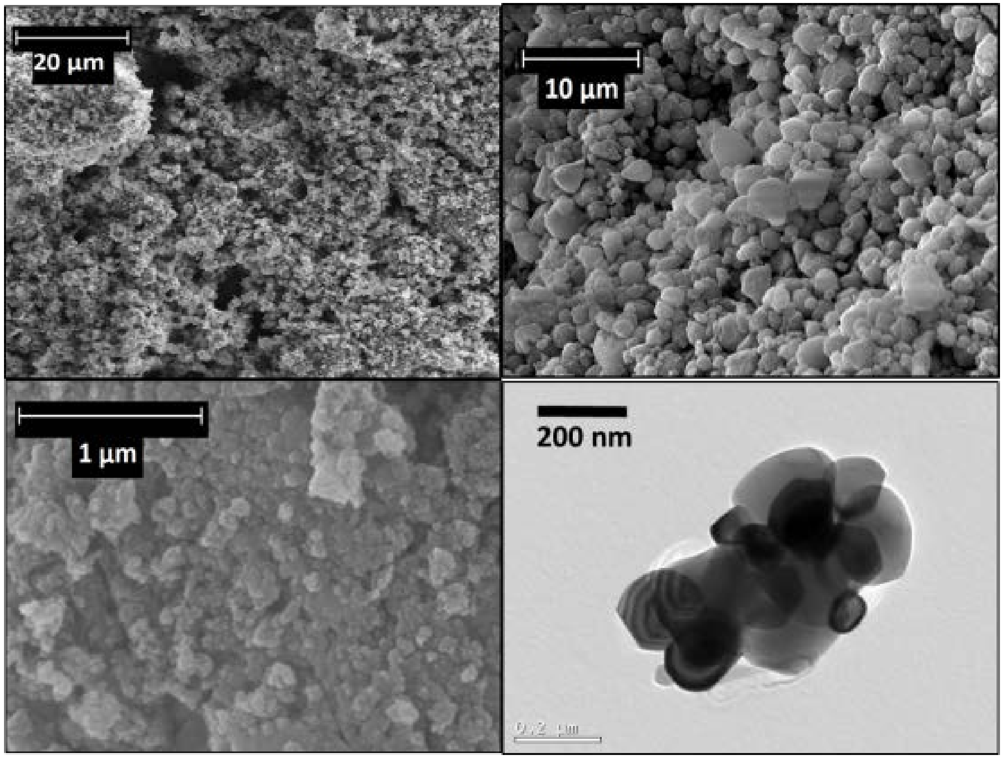
High energy mechanical mill (HEMM)

MX → **Silicon precursor**
B → **Reductant**

Silicon powder obtained after etching

Technical accomplishments (FY-12)

HSA-Si: SEM/TEM Characterization



Other approaches for generatingSi nanoparticles

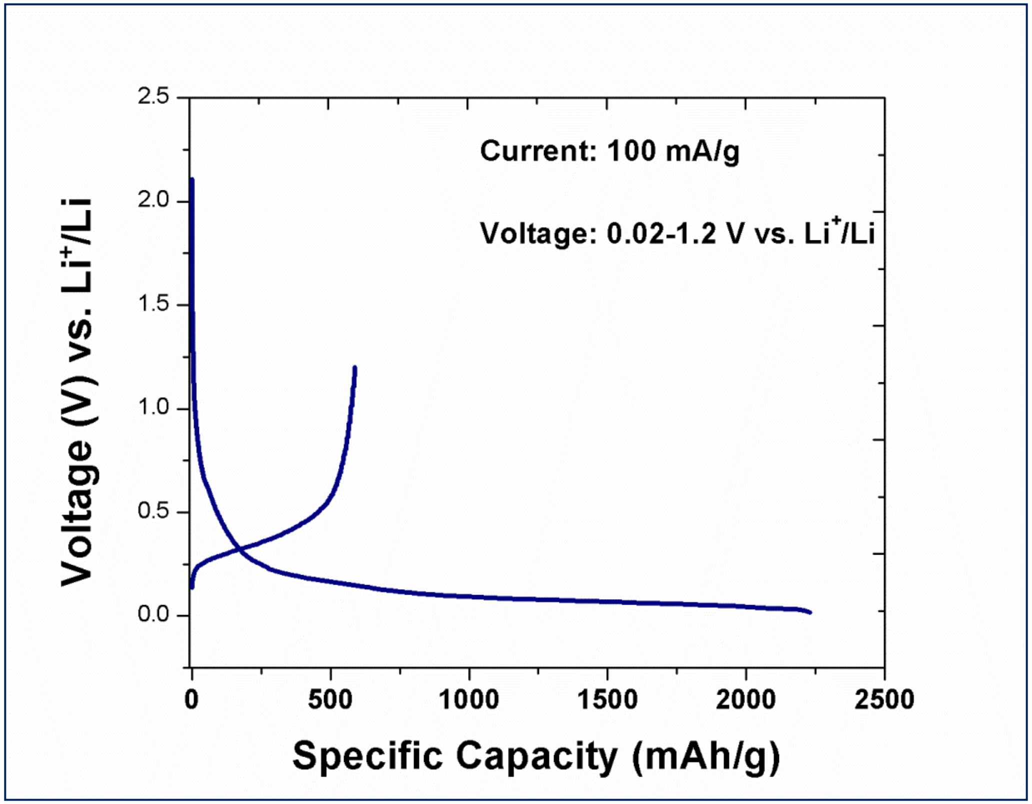
Method	Surface area (m^2/g)
Mechanical Milling[1]	100 m^2/g
Microwave plasma[2]	69 m^2/g

1. Russo et al,*Materials*, **4**, 1023 (2011)
2. Bywalez et al, *Nanoscale Res Lett*, **7**, 1 (2012)

- **Particle size range from 100 nm to 1 µm (wide distribution due to HEMM) with specific surface area corresponding to 190 m^2/g**
- **Higher surface area compared to other high throughput approaches for generating silicon nanoparticles**
- **Facile, scalable and high throughput approach for generating kilogram quantity HSA Si**

Technical accomplishments (FY-12)

HSA-Si: Preliminary Electrochemical Characterization



Electrolyte: 1M $LiPF_6$ in EC:DEC=1:2
Current : 100 mA/g (~C/2.5)
Voltage: 0.1 – 1.2 V vs. Li^+/Li

- **Loading:** 2.8 mg/cm^2

- **1st Discharge: 2230 mAh/g**
- **1st Charge: 590 mAh/g**
- **FIR loss: 73%**
- **Coloumbic efficiency: 97%**

- **Large FIR loss due to SEI formation on the large surface area of Si**

Future Work

Approach to decrease FIR → explore SCA and SECA coatings on the HSA-Si to decrease SEI formation

Technical Accomplishments (FY-12)

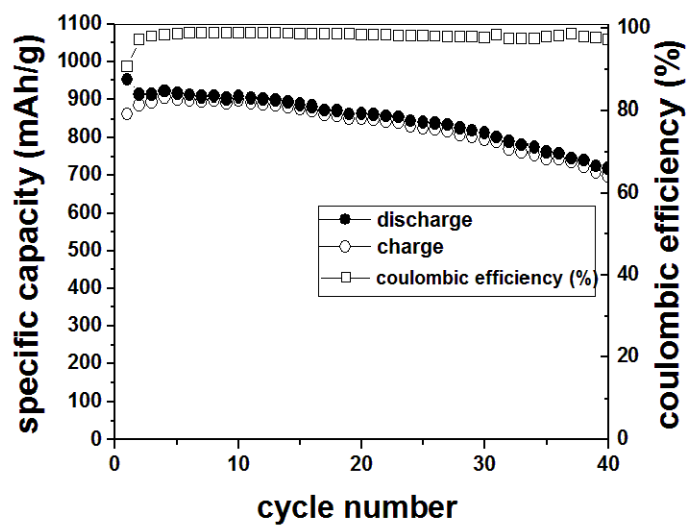
Development of higher fracture strength binder

Commercial binder: **5-10 wt.% PVDF**

Disadvantages of PVDF

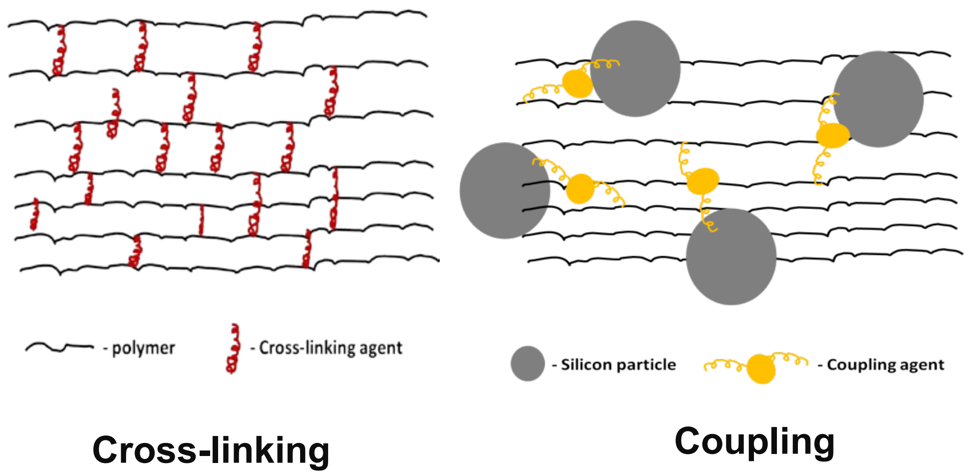
- No crosslinking within polymer
- Lower elasticity
- No bonding of Si with PVDF

Si-30%/C composite with PVDF binder



Loading: ~2.5mg/cm^2,
Cycled at **~80mA/g (~C/11 rate)**, 0.02V-1.2V
FIR loss: ~10%, 2nd cycle rev. capacity **~900mAh/g**
fade in capacity**: ~0.6% per cycle,** CE **~ 99.9%**

Approach to improve the binder strength

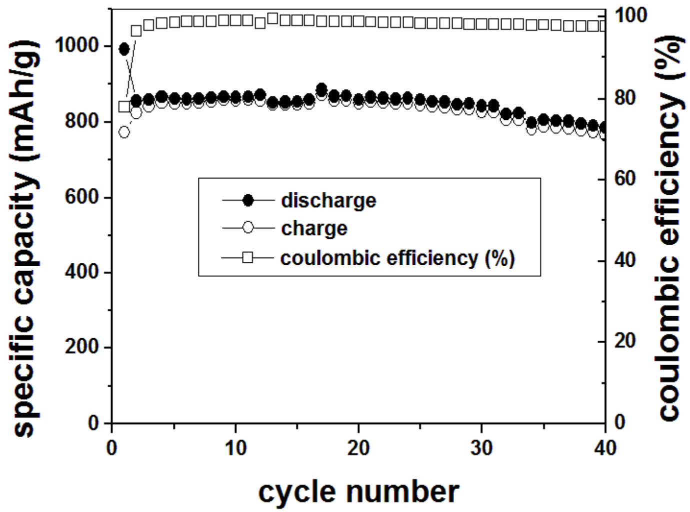


Attributes :

- Higher fracture strength of the binder
- Better elasticity and conductivity
- Cross-linking and coupling agents to enhance binding capacity

Technical Accomplishments (FY-12)
Development of higher fracture strength binder

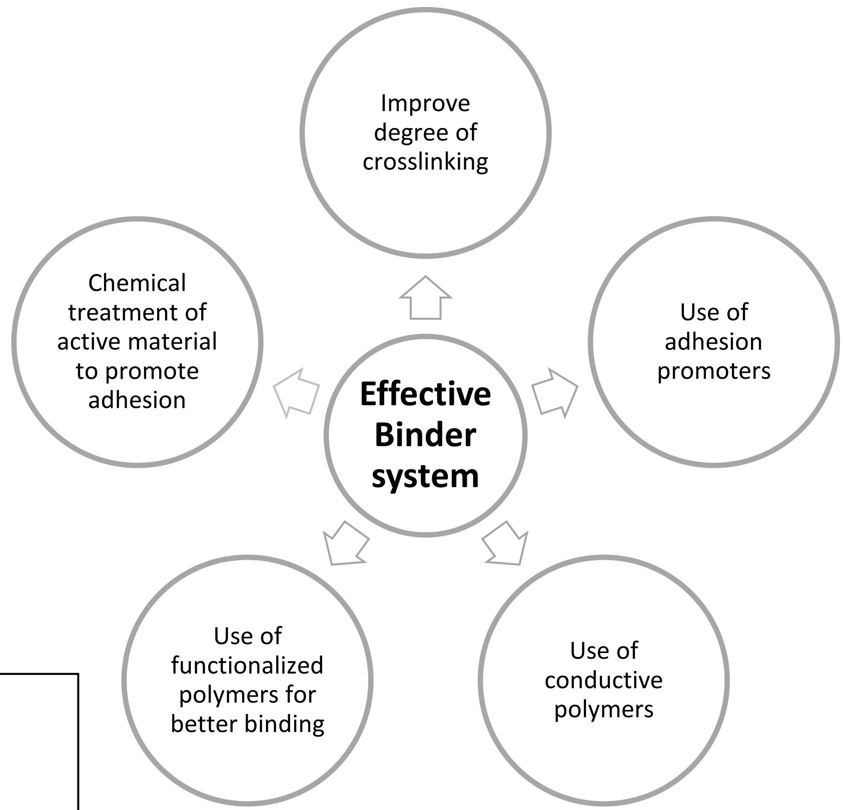
Cycling performance of Si-30%/C composite using novel synthesized high strength binder



Loading: ~2.5mg/cm²
Cycled at **~160mA/g (C/5 rate), 0.02V-1.2V**
FIR loss: ~20%, 2nd cycle rev. capacity **~820mAh/g**
fade in capacity:~**0.2% per cycle**, CE **~99.9%**

- Improved cyclability **(~34%)** with respect to PVDF binder
- Better adhesion of Si/C with this novel binder
- The synthesized binder exhibits higher strength

Future Direction of Research



Collaborations

Industry

- **Ford Motor company**, Detroit, MI

National Laboratory:

- **LBNL*** (Vince Bhattaglia); **ANL*** (Chris Johnson), **NETL*** (Ayyakkannu Manivannan)

University*:

- **University of Pittsburgh** (Spandan Maiti)

*Collaborators within the VT Program

Future work

- **SCA and SECA coatings** to be performed on the Silicon hollow Structures to improve CE, cycling stability and reduce FIR using:
    - CVD of SCA and SECA precursors
    - Explore coating strategies using a variety of cost effective methods
- Develop SCA and SECA composite on the HEMM derived **high specific surface area Silicon (HSA-Si)** to improve cyclability and coulombic efficiency
- Develop SCA and SECA coatings on electrodeposited *a*-Si films
- Improve electrochemical cycling of **1-Dimensional Si** network electrodes
- Modify the developed high strength binder to **enhance crosslinking and coupling** to Si/C composite
- Coin cell and pouch cell configuration with suitable cathode
- Bench marking of performance with baseline commercial Si identified by LBNL

Summary

- Approaches to generate large scale quantities of high performance amorphous Si (*a*-Si) and nanocrystalline Si (*nc*-Si) indicate promising electrochemical response.
  - Hollow Silicon nanostructures show **1800 mAh/g** with **76%** capacity (**Fade rate=0.32%loss/cycle**) retention at the end of **75 cycles at 2A/g**
  - CNT/Si heterostructures with interface control deliver capacities (>**1250 mAh/g**) with improved cycling stability (85% capacity retention at end of 75 cycles, **Fade rate=0.2%loss/cycle**)
  - Amorphous Si by electrodeposition showed a high capacity of **1300 mAh/g** with excellent stability for 100 cycles (**Fade rate=0.016%loss/cycle**)
  - Low first cycle irreversible loss (<10-16%) have been achieved
  - Excellent coulombic efficiency (~99.5-99.8%) has been attained
  - Facile, scalable approach to nanocrystalline high surface area Si
- Project initiated on generation of novel thermoplastic binders.
  - Cycling results on Si/C composite with the identified **high strength** binder indicate **better capacity retention** compared to **PVDF**

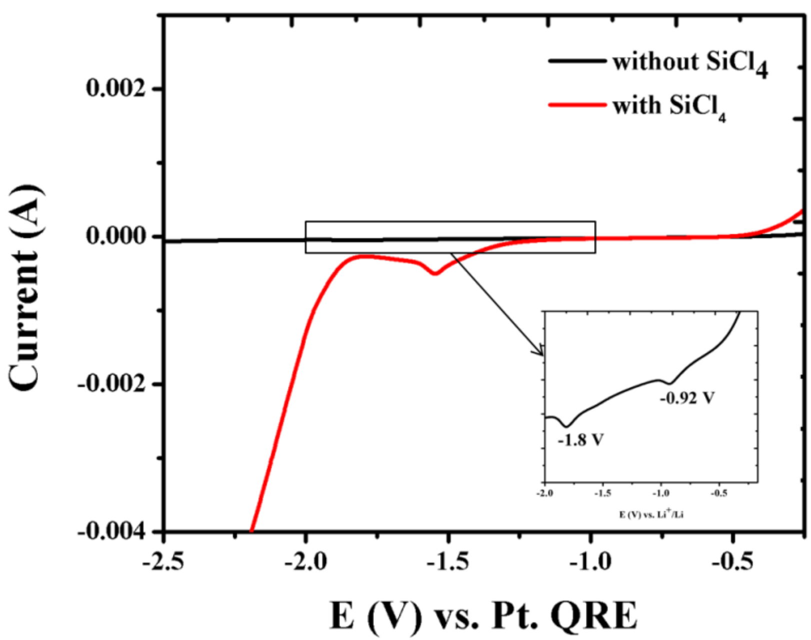
Technical Back-up Slides

Technical accomplishments (FY-12)

Amorphous Si by Electrodeposition from Silicon Halides

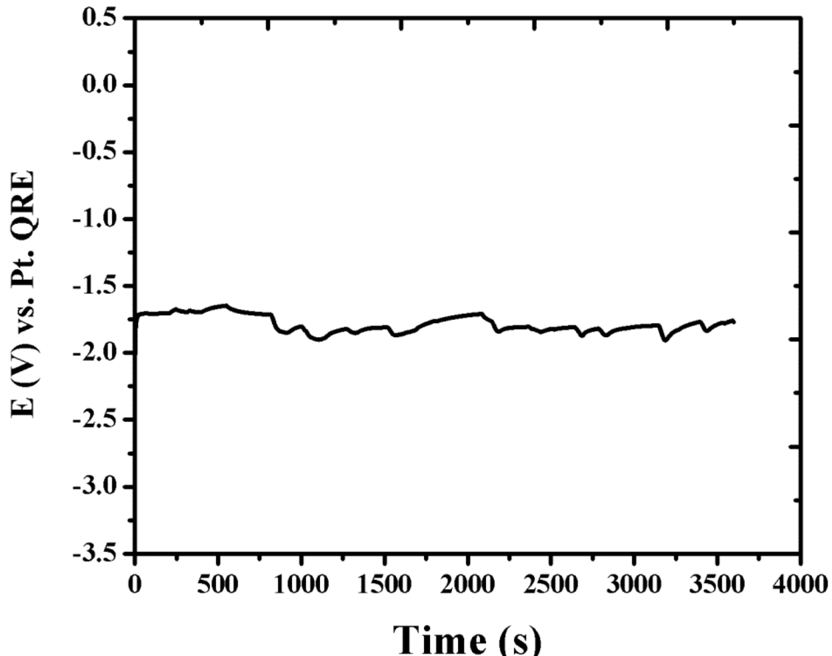
$$SiCl_4 + 4e^- \rightarrow Si + 4Cl^-$$

Working Electrode: Cu foil, Counter and Reference electrode: Pt
Electrolyte: 0.5M $SiCl_4$ + 0.1M TBACl in PC
TBACl: Tetrabutyl ammonium chloride, PC: Propylene carbonate



Linear Sweep Voltammetry

- **Sweep rate: 10 mV/s**
- **Si reduction at -1.6 V**

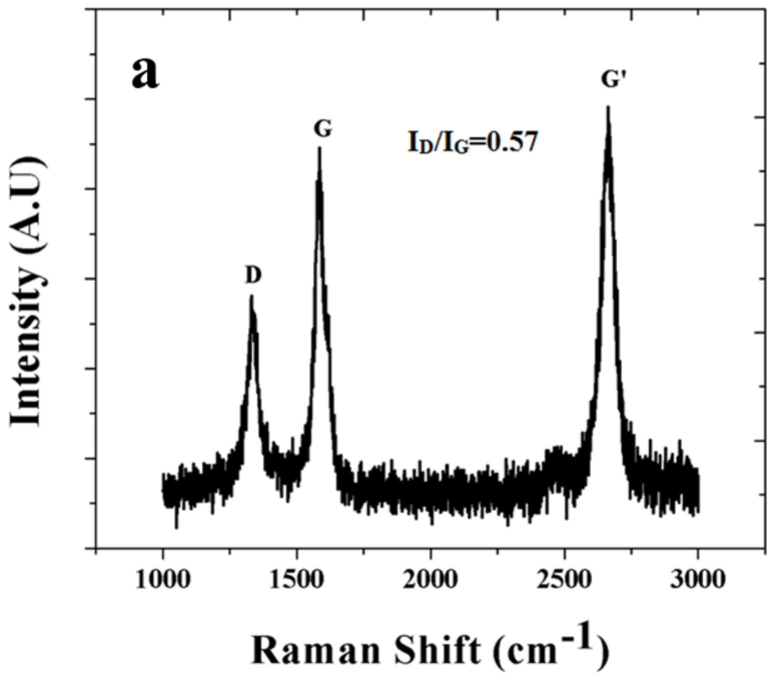


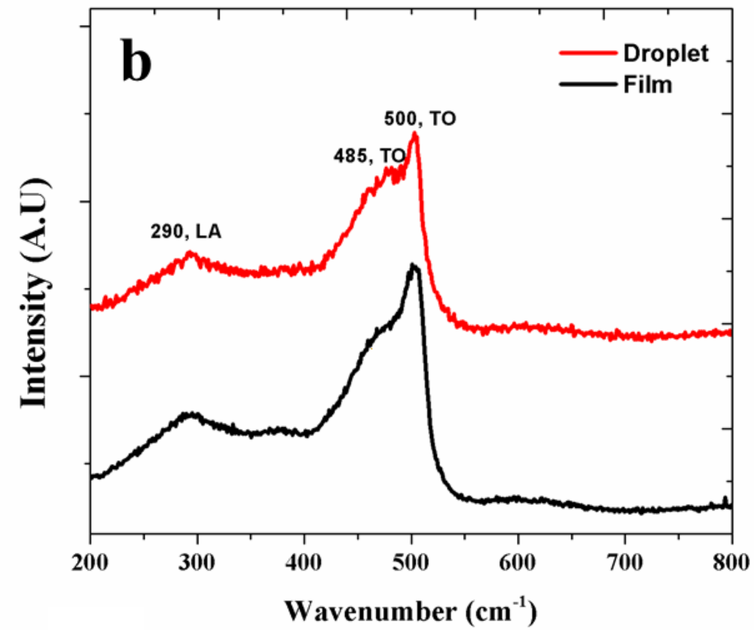
Choronopotentiometry

- **Applied Current Density: -1mA/cm^2**
- **Deposition Time: 1h**

Epur et al., 2012, *MSEB* , 177, 14, pg-1151

Engineering of *nc*-Si/CNT Heterostructures by CVD



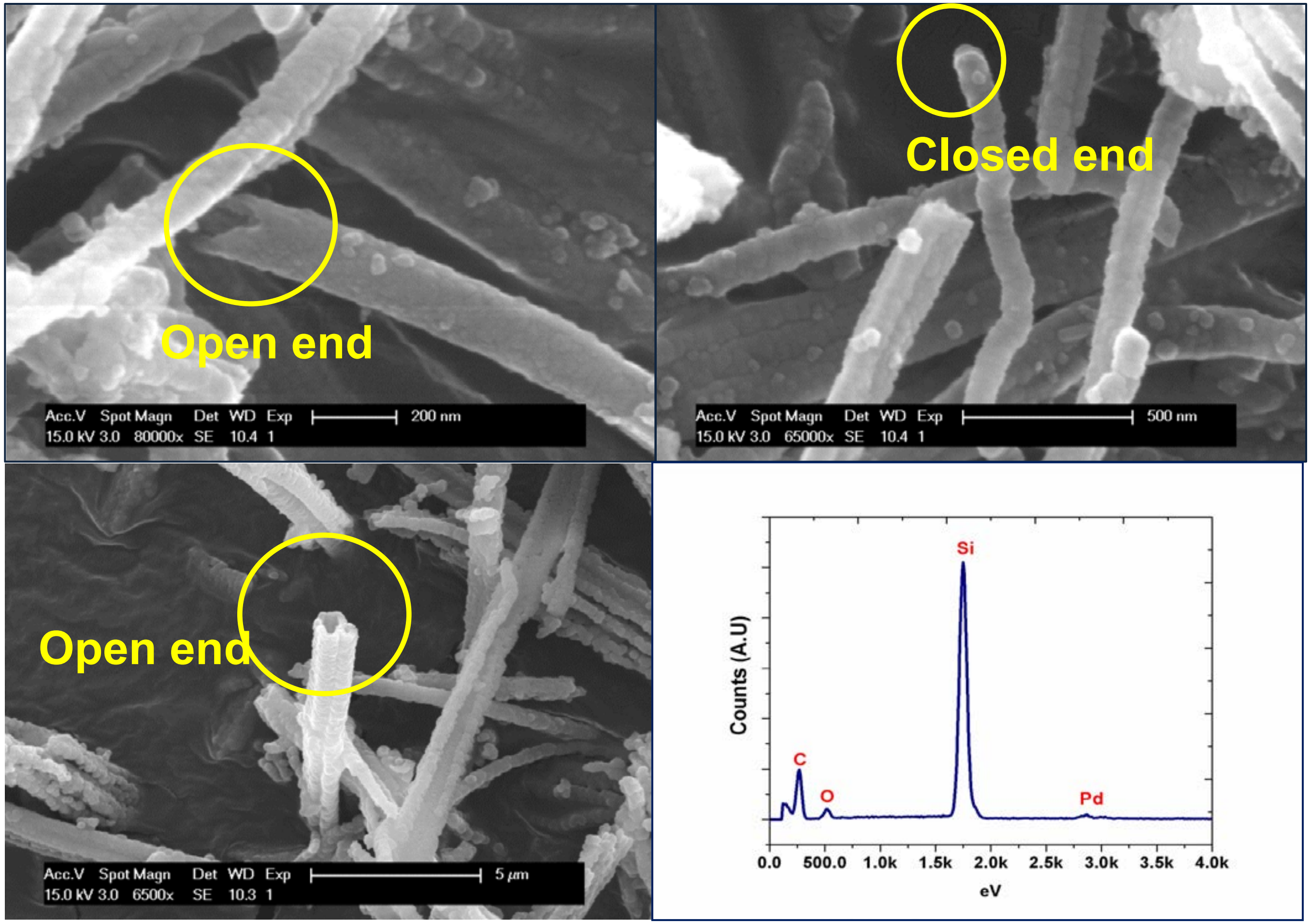


- Less disordered VACNTs
- nc-Si with some amount of a-Si by CVD of SiH_4

Epur et al., 2012, *Electrochim Acta.* 85, pg-680

Technical accomplishments (FY-12)

Si Hollow Structures: Hollow Si Structures after template dissolution (SEM)



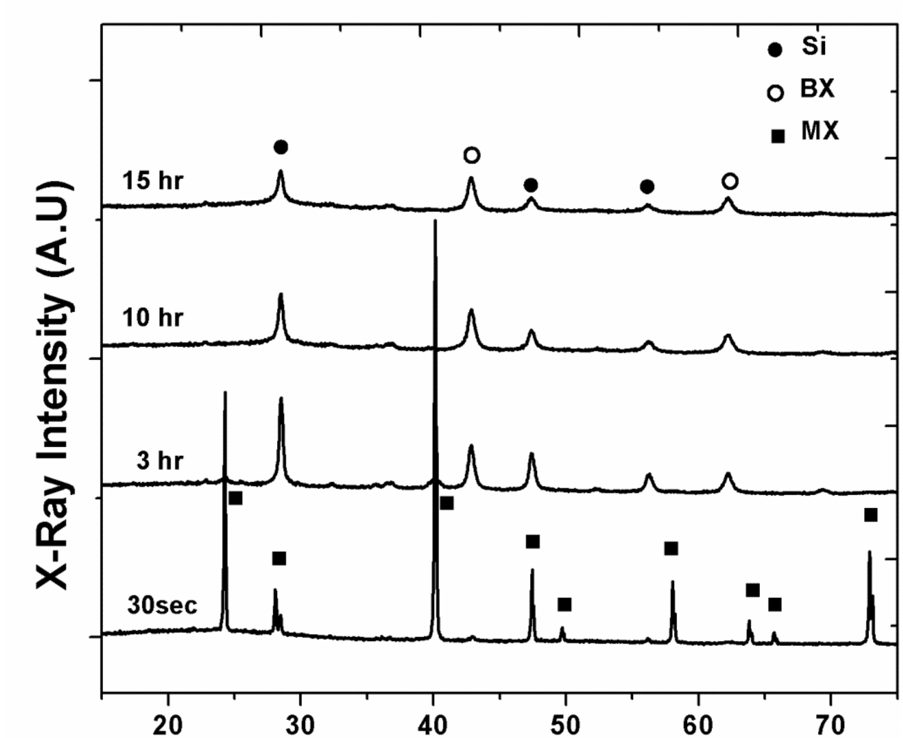
- Average Silicon coating thickness: 100-150 nm

Technical accomplishments (FY-12)

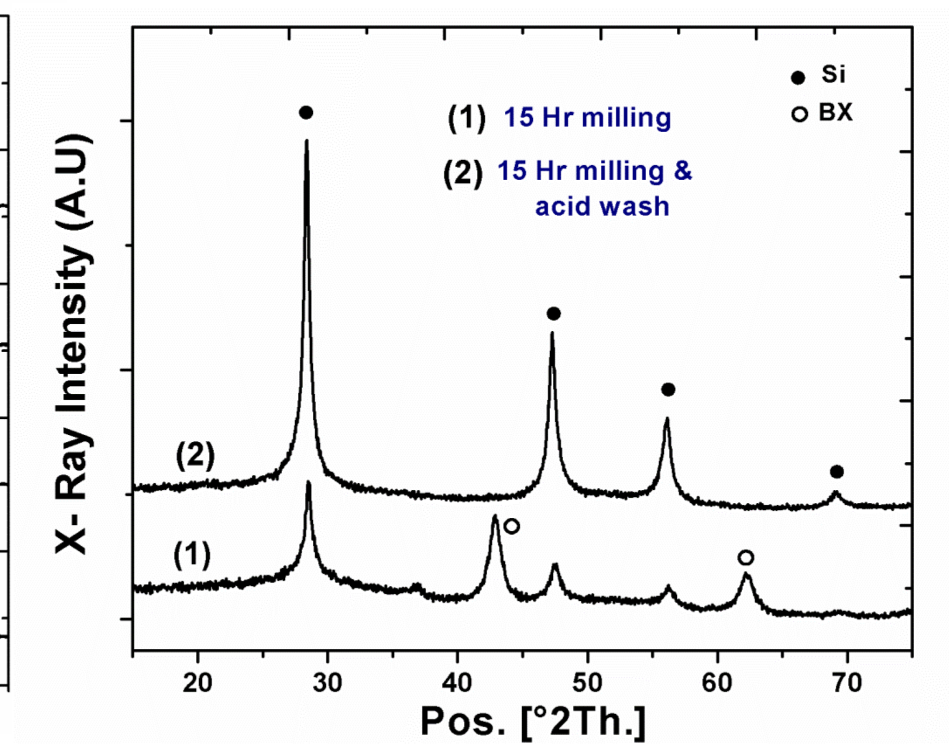
Facile, High through-put Scalable Approach to

High Specific Surface Area Si (HSA-Si)

Milling Kinetics



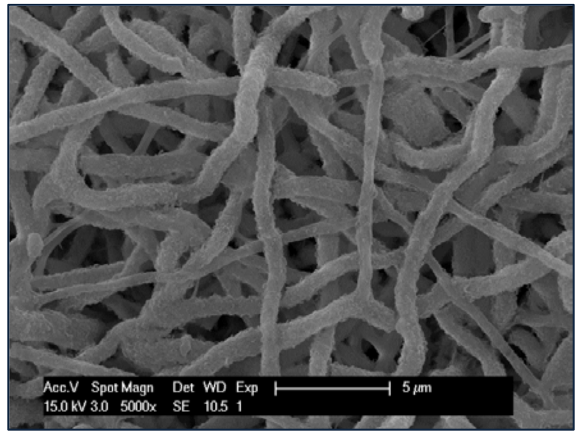
After acid etching



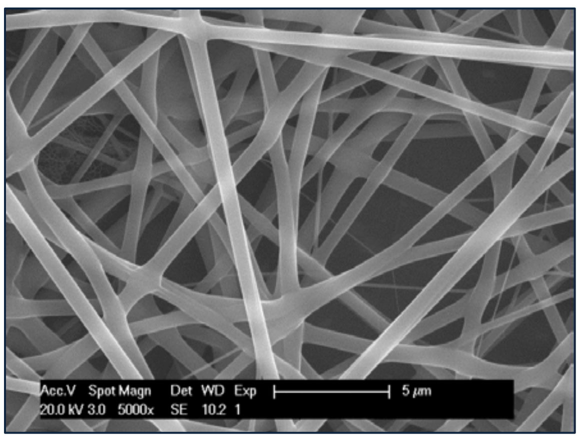
- Silicon precursor is completely reduced at the end of 15 h of mechanical milling
- Acid wash and etching removes the by-products and decreases the particle size
- Crystallite size: 20 nm from Debye Scherrer calculation (from Lorentzian contribution and eliminating strain)

Technical Accomplishments (FY-12)

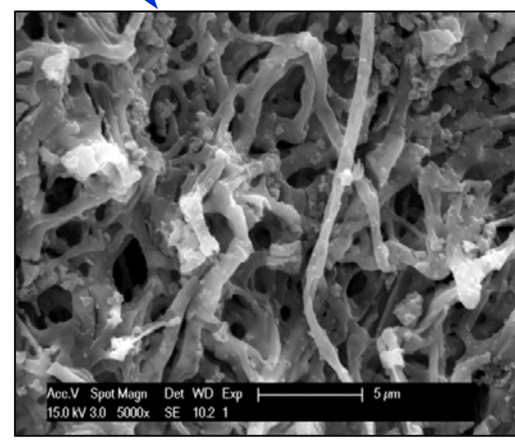
Novel Scalable Synthesis of 1-D Si Network Electrodes



Processed 1-D network



As-synthesized 1-D sacrificial network



1-D Si network after template dissolution

Through-put

- Generation of approximately 10g/h of the sacrificial network
- Amenable for direct fabrication of 1-D Si morphologies directly on current collector